

THE CRYSTAL STRUCTURE OF BOEHMITE

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Abstract—The crystal structure of a synthetic boehmite sample has been refined to an R of 0.047 in the space group $A2_1am$ from X-ray powder diffraction data. Inclusion of hydrogen atoms and/or refinement in the space group $A2_1am$ gave poorer results. Cell dimensions were determined as $a = 3.6936 (\pm 0.0003)$, $b = 12.214 (\pm 0.001)$, $c = 2.8679 (\pm 0.0003)$ Å. All Al–O(OH) distances lie between 1.88 and 1.91 Å. Shared octahedral edges are 2.51–2.52 Å, and unshared octahedral edges are 2.86–2.87 Å, in excellent agreement with those for layered silicates. The O–H . . . O distance between contiguous octahedral sheets is 2.71 Å. The computed X-ray pattern matches closely with the experimental pattern, indicating the degree to which the crystal structure has been determined.

Key Words—Boehmite, Crystal Structure, O–OH Distances, Powder X-ray Diffraction, Synthesis

INTRODUCTION

The crystal structure of boehmite, $AlO(OH)$, has been studied only by X-ray powder diffraction since sufficiently large single crystals, either natural or synthetic, are unknown. The general attributes of the boehmite structure, space group $A2_1am$ with $Z = 4$, were determined from synthetic materials by Reichertz and Yost (1946), who based their analysis on the structure of lepidocrocite, $FeO(OH)$, an isomorph of boehmite. The structure of lepidocrocite was determined by Ewing (1935) from oscillation and rotation photographs of a naturally occurring single crystal. The powder data of Reichertz and Yost (1946) were limited to 10 useful reflections, and their structure suggested a large Al–O distance, 2.06 Å, and a small O–H . . . O distance, 2.47 Å, smaller than any similar distance previously known.

Milligan and McAtee (1956) investigated the diffraction patterns of several synthetic boehmites, two of which were prepared hydrothermally. They presented a detailed listing of calculated and observed d-values and intensities and suggested $A2_1am$ as the most likely space group. Their structure showed one rather large Al–O distance of 1.99 Å, and an O–H . . . O distance of 2.70 Å between neighboring octahedral sheets.

An X-ray study of boehmite prepared by reaction of steam on aluminum at 220°C was reported by Bezjak and Jelenic (1964). They suggested that the space group may be $C22_2$, $Pnna$, or $Pbcn$, but indicated $A2_1am$ as the most probable. They used least squares and Fourier methods to refine the atomic coordinates and anisotropic temperature parameters and obtained an R of 0.05 for an unspecified number of reflections. Their structure showed an Al–O distance of 1.94 Å and an O–H . . . O distance of 2.63 Å.

Recently, Christensen and Christensen (1978) reinvestigated the structure of lepidocrocite by neutron powder diffraction. The best agreement between observed and calculated intensities was obtained when the structure was refined in the space group $Cmc2_1$ ($= A2_1am$), an acentric variation of $A2_1am$. The lower space-group symmetry was a result of the noncentered location of the hydrogen atoms. The data recorded at room temperature gave 16 resolved peaks with contributions from 108 reflections and refined to an R of 0.13.

One objective of our investigation of the synthesis and characterization of boehmite was to determine the atomic coordinates as accurately as possible. The conflicting nature of the previous studies led to an examination of the data for boehmite given in the J.S.P.D. Data File (starred card number 21-1307). The data on this card are not satisfactory for several reasons. Two errors are noted; Z was incorrectly given as 2, and two adjacent d-values were indexed as (320). The d-value of 0.9818 Å was unindexed, and little distinction was made between intensities whose values were small, e.g., 17 reflections were listed with an intensity equal to 2 on a scale of 100 = strongest, while 5 reflections were recorded with intensity <2. We attempted to refine these data in space group $A2_1am$ with correct (hkl) values and with intensities having values <2 given a value of unity. Refinement of the structure gave an R of 0.10, but gave an unreasonably large Al–O distance of 2.14 Å and a rather small Al–OH distance of 1.80 Å.

Our inability to extract satisfactory atomic coordinates for boehmite from the literature prompted us to record our own X-ray powder data and to refine both the cell dimensions and the atomic coordinates. Refinement was attempted in the space groups $A2_1am$ and $A2_1am$ with and without the presence of hydrogen atoms. We also analyzed the limits of error in all of the derived parameters. This information was not given or not presented in a quantitative manner in any of the previous studies.

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EXPERIMENTAL

Boehmite was synthesized by the method presented by Hsu (1967). Briefly, 100 ml of a 0.6 N NaOH/4 N NaCl solution was added dropwise over a period of 30 minutes to 100 ml of 0.2 M AlCl₃. The resulting gelatinous precipitate was washed by successive dilutions with water and alcohol and centrifuged until chloride-free as determined with silver nitrate solution. The precipitate was then placed in a silver-lined hydrothermal bomb and held at 300°C for 6 days after which the material was freeze-dried, ground for 15 minutes in a mechanical mortar, and stored in a stoppered vial in a desiccator prior to recording the diffraction pattern.

The X-ray mount was prepared by back-loading the boehmite powder into an aluminum holder. Experimentation showed that the X-ray pattern was unaffected by the type of mount, whether front or back-loaded, or the amount of pressure used in loading the powder, *i.e.*, preferred orientation was not evident, owing, perhaps, to the intergrown nature of the small crystallites as seen by scanning electron microscopy (Hofmann, 1978). The sample length was large enough to contain the X-ray beam at the smallest diffraction angle, and the volume of sample irradiated was virtually constant at all diffraction angles.

The experimental conditions were as follows: 1° divergence and anti-scatter slits, 0.006" receiving slit; scanning speed ½°2θ/min, time constant 2; scale factor 16 and multiplier 1; chart speed ½ in/min. Power settings of 35 kv and 8 ma were used between 10 and 74°2θ and 50 kv and 20 ma for the region from 51 to 159°2θ. The pattern (Figure 1, lower trace) was taken with Ni-filtered Cu radiation on a Philips diffractometer equipped with a scintillation detector and pulse-amplitude discrimination. The positions of the diffraction maxima were corrected over the entire angular range by comparison with those of a powdered silicon sample supplied by Philips. The intensities of the peaks in the overlap region provided an average figure which was used to place all of the intensities on a common scale. The intensities were taken as the planimetered area under the peaks after drawing in a suitable background. Observed d-values and intensities for each (hkl) are listed in Table 1.

CELL DIMENSION REFINEMENT

The reflections were indexed on the basis of an orthorhombic cell, and the cell dimensions were refined in a least-squares program. The relationship of d-value, (hkl), and cell dimensions for an orthorhombic cell was treated as a linear equation in the variables 1/a², 1/b², and 1/c². The quantity minimized was the sum of the squares of the differences between the observed and calculated values of 1/d². Standard deviations of the refined cell dimensions were derived from the diagonal terms of the inverted matrix. Solution of the normal

Table 1. Observed and calculated d-values, observed intensities, and observed and calculated structure factors for boehmite.¹

hkl	d _o (Å)	d _c (Å)	I _o	F _o	F _c
020	6.14	6.11	1000	169	-164
120	3.168	3.161	416	155	-151
031 (140)	2.349	2.345	328	192	189
131	1.981	1.980	33	53	-57
051	1.861	1.860	243	217	-220
200	1.848	1.847	163	254	-254
220	1.768	1.768	45	99	102
151	1.661	1.661	94	110	-116
080	1.527	1.527	36	151	-153
231	1.450	1.451	95	130	-133
002	1.434	1.434	51	194	197
180	1.411	1.411	2	29	-28
022	1.396	1.396	15	76	-82
171	1.382	1.382	64	113	116
260	1.368	1.368	2	30	-30
251	1.311	1.310	139		
122	1.303	1.306			
091	1.225	1.227	11		
142		1.225			
0,10,0	1.223	1.221			
320	1.207	1.207	12	79	83
280	1.176	1.177	23	115	115
1,10,0 (271)	1.160	1.160	29		
202	1.133	1.133	39	154	-146
222	1.114	1.114	12	60	63
331	1.090	1.090	2	26	33
082	1.045	1.045	14	95	-97
0,11,1	1.036	1.036	1	26	-38
351	1.027	1.027	13	65	63
2,10,0 (0,12,0)	1.019	1.019	7		
262	0.9902	0.9898	4	37	-26
1,12,0	0.9817	0.9813	6	64	-67
371	0.9494	0.9493	17	73	-72
033	0.9309	0.9307	14		
0,10,2		0.9298			
400		0.9235			
322	0.9234	0.9235	21		
113		0.9229			
420	0.9131	0.9131	5	55	-46
282	0.9099	0.9097	26	85	78
2,11,1	0.9036	0.9032	5	39	31
133	0.9017	0.9025	29		
1,10,2		0.9017			
342		0.8933			
0,13,1	0.8931	0.8929	26		
2,12,0	0.8913	0.8914			
053	0.8904	0.8903	38		
391	0.8691	0.8690			
1,13,1	0.8683	0.8679			
3,10,0	0.8673	0.8672	20	68	64
153	0.8656	0.8655			
431	0.8591	0.8593	32		
233	0.8310	0.8311			
2,10,2	—	0.8305			
0,12,2	—	0.8300	36	81	-73
451	0.8270	0.8271			
173	0.8175	0.8176	15	50	55
1,12,2	0.8097	0.8098	12	42	-47
2,13,1	0.8036	0.8039	19	51	-49
253	0.8018	0.8020	48	74	69
480	0.7901	0.7902	19	63	-59
3,12,0	0.7843	0.7845	10	41	44

¹ Structure factors are given only for those reflections utilized in the structure refinement.

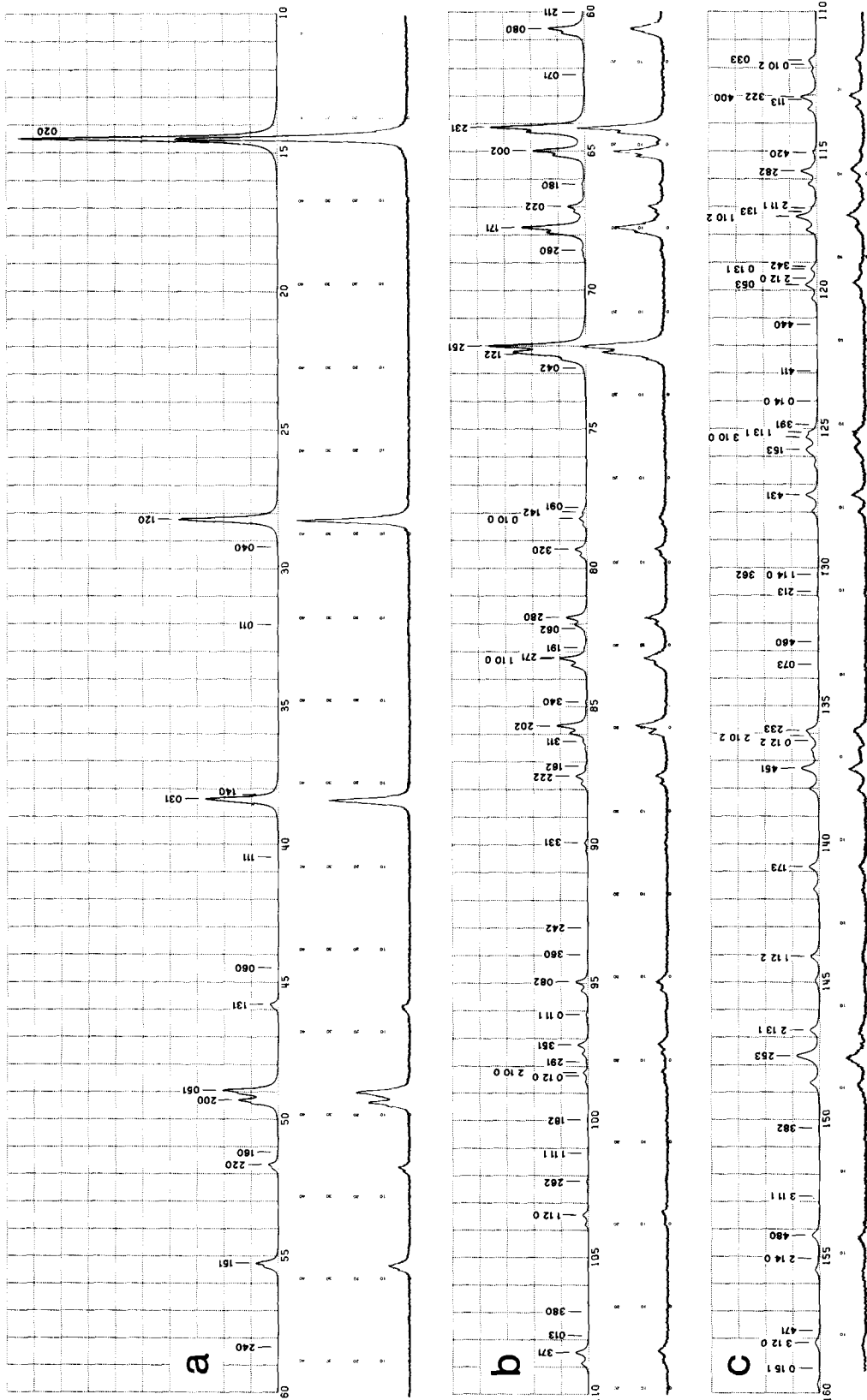


Figure 1. Calculated and experimental X-ray powder diffraction traces of boehmite for Cu radiation. Computer-generated pattern is shown as upper trace and experimental pattern is shown as lower trace. (a) $10-60^{\circ}2\theta$, (b) $60-110^{\circ}2\theta$, (c) $110-160^{\circ}2\theta$. Vertical scale of (a) is approximately 4.5 times that of (b) and (c) with vertical scale of calculated pattern chosen to approximate that of observed pattern. Grid spacing for computed pattern originally was 1 inch. Indexing is shown at calculated position of 2θ for each (hkl) for $K\alpha_1$ radiation. The Cauchy constant for computed peaks is 14.0 deg^{-1} .

Table 2. Cell dimensions for boehmite.

	RY	MM	BJ	This study
a (Å)	3.691	3.69	3.700	3.6936 (± 0.0003)
b (Å)	12.24	12.24	12.227	12.214 (± 0.001)
c (Å)	2.859	2.86	2.868	2.8679 (± 0.0003)

RY = Reichertz and Yost (1946), MM = Milligan and McAtee (1956), BJ = Bezjak and Jelenic (1964).

equations yielded the results shown in Table 2. Only nonmultiple reflections and/or reflections whose d-values could be read with certainty were included. Thirty-three reflections with equal weight were used.

CRYSTAL STRUCTURE REFINEMENT

Atomic positions and isotropic temperature factors were refined by standard three-dimensional least-squares techniques using the CRYM crystallographic computing package (DuChamp, 1964). Initial coordinates were the "ideal" coordinates of Reichertz and Yost (1946) who derived them from an application of Pauling's Rules. Initial B-values were chosen as 0.5 for Al and 1.0 for O and OH. A starting B-value of 3.0 was chosen for the hydrogen atom when it was included. All nonmultiple reflections were used in the refinement, and equal weights were given to all reflections. We considered the inclusion of the multiple (031)/(140) reflection to be justified here as the (140) peak made a negligible contribution to the intensity of this reflection. Scattering factors for fully ionized atoms were taken, for the most part, from volume 4 of the International Tables for X-ray Crystallography with the real component of the anomalous dispersion correction included. The scattering factor for O^{2-} was taken from Suzuki (1960). The hydroxyl group was approximated as O^- regardless of whether the hydrogen atoms were included or not. The parameters varied in the refinement were the y-coordinates of three atoms, their corresponding B-values, and the scale factor.

The function minimized in the least-squares refine-

Table 3. Atomic coordinates for boehmite for space group Amam and isotropic temperature factors.

Atom	RY	MM	BJ ¹	This study	
	y	y	y	y	B
Al	-0.334	-0.322	-0.3165	-0.317 (± 0.001)	1.2 (± 0.1)
O	0.287	0.291	0.2925	0.286 (± 0.002)	1.9 (± 0.4)
OH	0.067	0.080	0.0765	0.080 (± 0.002)	1.4 (± 0.3)

The x and z coordinates for the three atoms listed are required by symmetry to be 0.25 and 0.00, respectively.

¹ Although reported with four significant digits with no estimates of reliability, the substantial anisotropy of the thermal ellipsoids raises doubt as to the accuracy and precision of these data.

RY = Reichertz and Yost (1946), MM = Milligan and McAtee (1956), BJ = Bezjak and Jelenic (1964).

ment was $\sum w |kF_o^2 - F_c^2|^2$, where w is the weighting factor which was set at unity for all reflections, k is a scale factor, and F_o and F_c are the observed and calculated structure factors, respectively. Standard deviations in the refined parameters were estimated from the diagonal terms of the inverted matrix from the final least-squares cycle.

DISCUSSION OF RESULTS

The (hkl) and calculated d-values shown in Table 1 are based on the refined cell dimensions determined in this study (Table 2). Cell dimensions reported in the earlier investigations are also shown in Table 2. The cell dimensions given in the J.S.P.D. Data File and those of Bezjak and Jelenic (1964) are identical. The largest difference noted is the b-dimension; our value is about 0.01 Å smaller than those previously reported.

Observed and calculated structure factors are tabulated in Table 1 for those reflections that were used in the crystal structure refinement in the space group

Table 4. Calculated d-values based on refined cell dimensions and calculated intensities based on $I_c(020) = 1000$ of boehmite for weak reflections not recorded experimentally.

hkl	$d_c(\text{Å})$	I_c
040	3.054	0.1
011	2.792	0.1
111	2.227	1.0
060	2.036	1.3
160	1.783	1.8
240	1.580	0.1
211	1.540	0.8
071	1.491	1.6
042	1.298	0.1
062	1.172	1.6
191	1.164	1.5
340	1.142	1.6
311	1.127	3.4
162	1.117	1.8
242	1.062	0.1
360	1.054	0.8
291	1.022	0.9
182	1.006	1.0
1,11,1	0.9970	0.1
380	0.9585	0.4
013	0.9531	0.2
440	0.8840	0.0
411	0.8768	0.3
0,14,0	0.8724	0.4
1,14,0	0.8491	0.1
362	0.8491	1.4
213	0.8470	0.3
460	0.8410	1.0
073	0.8384	0.2
382	0.7969	1.0
3,11,1	0.7925	0.2
2,14,0	0.7889	1.3
471	0.7851	0.6
0,15,1	0.7833	0.0

Table 5. Interatomic distances of boehmite in Ångstrom units.

	RY	MM	BJ	This study
Cation-anion distance:				
Al-O	2.06	1.99	1.898	1.91 (± 0.02)
Al-O	1.94	1.88	1.876	1.88 (± 0.01)
Al-OH	1.88	1.87	1.940	1.91 (± 0.01)
Shared edge:				
O-O	2.51	2.54	2.561	2.51 (± 0.01)
O-OH	2.69	2.58	2.655	2.52 (± 0.02)
Unshared edge:				
O-O	2.86	2.86	2.868	2.87 (± 0.00)
O-OH	2.94	2.82	2.844	2.86 (± 0.01)
Interlayer:				
O-H . . . O	2.47	2.70	2.630	2.71 (± 0.01)

RY = Reichertz and Yost (1946), MM = Milligan and McAtee (1956), BJ = Bezzak and Jelenic (1964).

Amam. Our atomic coordinates and those of the earlier investigations are set forth in Table 3.

A list of permissible reflections in space group Amam either unobserved or overlapped by more intense reflections is given in Table 4. Most of these reflections have a computed intensity of about 1/1000 of that of the most intense reflection (020). The most intense of these weak reflections is the (311) reflection which occurs at about $86^\circ 2\theta$; it is overlapped by the (202) reflection, but is barely discernible on the experimental pattern, Figure 1 (lower trace). Owing to geometrical limitations in the experimental apparatus we were unable to record reflections above $159^\circ 2\theta$. Two Bragg maxima are expected at angles $> 159^\circ 2\theta$ for Cu radiation, and our data predict that one of these, the (402) reflection, should be intense enough to be observed, while the (093) reflection should be too weak to be observed.

The final R was 0.047 after 3 cycles in the least-squares refinement for the structure in space group Amam in which no allowance was made for hydrogen atoms. Inclusion of hydrogen atoms and/or refinement in the space group $A2_1am$ invariably led to a higher value of R. Holm *et al.* (1958) indicated that the O-H . . . O bond in boehmite was asymmetric on the basis of their NMR analysis. They suggested that a reinterpretation on the basis of the acentric space group $A2_1am$ was in order. However, they noted that if "the structure was disordered in such a way that the polarity of each infinite O-H . . . O chain bears no relation to the polarity of neighboring chains, . . . the effective space group could be centric." Our findings do not indicate an acentric space group.

Pertinent atomic distances computed from our coordinates and distances computed from coordinates found in previous studies are given in Table 5. Our Al-O(OH) distances are more consistent (1.88–1.91 Å) than those of any previous study. The lengths of the shared octahedral edges are 2.51–2.52 Å, while those of the unshared edges are 2.86–2.87 Å, both in excellent

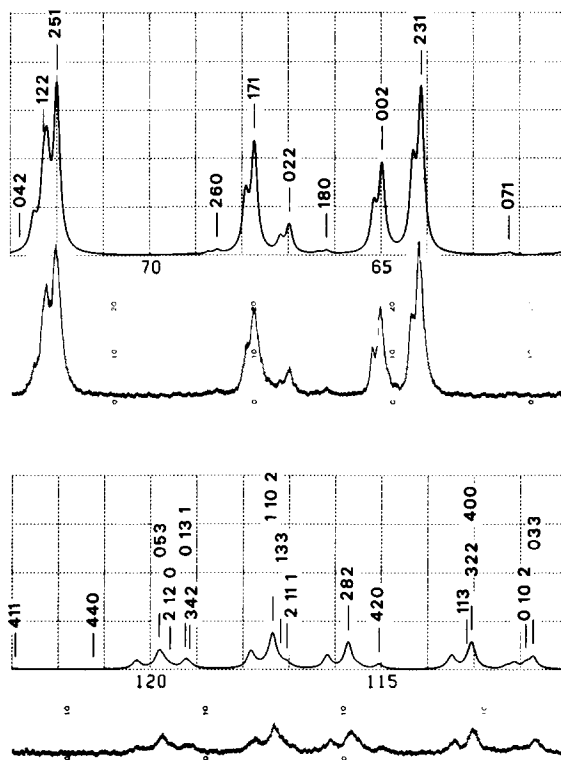


Figure 2. Detail of Figure 1 between 61° and $73^\circ 2\theta$ and between 111° and $123^\circ 2\theta$.

agreement with comparable dimensions in similar structures, *i.e.*, layered silicates. The O-H . . . O distance between neighboring octahedral sheets is 2.71 Å, significantly larger than the 2.47 Å originally reported by Reichertz and Yost (1946) and larger than the 2.63 Å indicated by Bezzak and Jelenic (1964), but virtually the same as that given by Milligan and McAtee (1956).

The degree to which the boehmite structure is known as determined in the present study is portrayed in Figure 1 where the entire experimental pattern and a computed pattern are shown together. The details of the program that generated the computed pattern will be published separately. Briefly, the calculated intensities based on the refined atomic coordinates were apportioned for each (hkl) value into a 2:1 ratio at the computed 2θ values for the wavelengths of Cu $K\alpha_1$ and Cu $K\alpha_2$. Intensities were calculated by means of the relationship $I_c = p|F|^2L$, where p is the multiplicity factor, F is the structure factor, and L is the powder Lorentz-polarization factor. Each intensity value was distributed by means of a Cauchy function, whose form is $[1 + c_c \cdot \Delta(2\theta)^2]^{-1}$, centered at the appropriate positions of $K\alpha_1$ and $K\alpha_2$ for each (hkl), and computed to a minimum angular distance of $10^\circ 2\theta$ on either side of the peak maximum. The constant, c_c , in the Cauchy function was determined empirically by estimating it from two of the reflections observed on the experimental

pattern. All peaks were further modified by an arbitrary broadening function whose form was $\sqrt{\cos \theta}$. The vertical scale of the computed pattern was chosen to approximate that of the experimental pattern. A portion of Figure 1 is enlarged in Figure 2 to enable the reader to judge better the level of agreement between the two traces.

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Резюме—Кристаллическая структура образца синтетического бемита была рафинирована до R равному 0,047 в пространственной группе Amam по данным порошкового метода рентгеноструктурного анализа. При включении водородных атомов и/или рафинировании в пространственной группе $A2_1$ am были получены худшие результаты. Были определены следующие размеры ячейки: $a = 3,6936 (\pm 0,0003)$, $b = 12,214 (\pm 0,001)$, $c = 2,8679 (\pm 0,0003)$ Å. Все расстояния Al-O(OH) лежат в пределах от 1,88 до 1,91 Å. Длина общих октаэдрических ребер 2,50-2,52 Å, длина необщих ребер 2,86-2,87 Å, в прекрасном соответствии с длинами ребер слойных силикатов. Расстояние O-H . . . O между смежными пластинами 2,71 Å. Вычисленная рентгеновская модель хорошо согласуется с экспериментальной моделью, что указывает до какой степени определена кристаллическая структура.

Resümee—Durch Röntgenpulverdiagramme wurde die Kristallstruktur eines synthetischen Boehmiten verfeinert bis zu R 0,047, in der Raumgruppe Amam. Einschluß von Wasserstoffatomen und/oder Verfeinern in der Raumgruppe $A2_1$ am ergab nicht so gute Resultate. Zelldimensionen wurden bestimmt: $a = 3,6936 (\pm 0,0003)$, $b = 12,214 (\pm 0,001)$, und $c = 2,8679 (\pm 0,0003)$ Å. Alle Al-O(OH) Abstände sind zwischen 1,88 und 1,91 Å. Gemeinsame Kanten sind 2,50-2,52 Å und nicht geteilte Kanten sind 2,86-2,87 Å, was gut mit den Werten von Schichtsilikaten übereinstimmt. Der O-H . . . O Abstand zwischen benachbarten oktahedrischen Platten ist 2,71 Å. Errechnete röntgenmuster stimmen mit den experimentellen Daten überein, was auf das Ausmaß hindeutet, zu dem die Kristallstruktur bestimmt wurde.

Résumé—La structure cristalline d'un échantillon d'une boehmite synthétique a été raffinée à un R de 0.047 dans le groupe d'espace Amam de données de diffraction aux rayons-X. L'inclusion d'atomes d'hydrogène et/ou le raffinement dans le groupe d'espace $A2_1$ am a donné de moins bons résultats. Les dimensions de maille ont été déterminées: $a = 3.6936 (\pm 0.0003)$, $b = 12.214 (\pm 0.001)$, et $c = 2.8679 (\pm 0.0003)$ Å. Toutes les distances Al-O(OH) se trouvent entre 1.88 et 1.91 Å. Les bords octaédriques communs sont 2.50-2.52 Å, et les bords octaédriques non-communs sont 2.86-2.87 Å, en excellent accord avec ceux des silicates interstratifiés. La distance O-H . . . O entre des couches octaédriques contigües est 2.71 Å. Le cliché de rayon-X calculé est très proche du cliché expérimental, indiquant le degré auquel la structure cristalline a été déterminée.